

A POSSIBLE SINK FOR METHANE ON MARS

Per Nørnberg¹, Svend J. Knak Jensen², Jørgen Skibsted², Hans J. Jakobsen², Inge L. ten Kate³, Haraldur P. Gunnlaugsson⁴, Jonathan P. Merrison⁴, Kai Finster⁵, Ebbe Bak⁵, Jens J. Iversen⁴, Jens C. Kondrup²,

¹Department of Geoscience, Høegh-Guldbergs Gade 2, Aarhus University, DK-8000 Aarhus C, Denmark.

²Instrument Center for Solid-State NMR Spectroscopy, Department of Chemistry, Center (iNANO), Aarhus University, Denmark, ³Department of Earth Sciences, Utrecht University, The Netherlands. ⁴Department of Physics and Aarhus University, Denmark. ⁵Department of Bioscience, Aarhus University, Denmark.

Introduction: Recently methane (CH₄) has been observed in the Martian atmosphere from a satellite orbiting the planet [1] as well as from Earth based telescopes [2]. A significant feature of methane concentrations is that they show a substantial time and spatial variation. Detailed recent snapshots measurements by MSL have shown that the concentration of methane is very low, *i.e.*, 0.18 ± 0.67 ppbv [3]. To reconcile these findings a fast destruction mechanism is required.

Here we show, using solid-state ¹³C and ²⁹Si magic-angle spinning NMR spectroscopies, that wind driven erosion produces highly reactive sites on mineral grain surfaces that sequester methane by forming covalent bonds with methyl groups and propose that this mechanism can be the hitherto undiscovered methane sink on Mars [4].

Materials and methods: The wind driven erosion of surface material is simulated using the specially designed apparatus depicted in Fig. 1. Commercially available quartz (Merck, 1.07536) was chosen as an analogue for surface material because of its simple chemical composition. The quartz was placed in a borosilicate flask with ¹³C-methane (Sigma-Aldrich, 490229, 99% enriched) to facilitate NMR investigations.

Results and discussion: The reaction of ¹³C-enriched methane with surface sites of highly active quartz particles is unambiguously demonstrated by the ¹³C{¹H} CP/MAS and ²⁹Si{¹H} CP/MAS NMR spectra shown in Fig. 2. In these spectra the cross-polarization (CP) NMR technique transfers ¹H magnetization to either the ¹³C or ²⁹Si spins *via* heteronuclear dipolar couplings and thereby acts as a filter for detecting only ¹³C and ²⁹Si spin nuclei within a distance less than 3-5 Å to nearby ¹H nuclei. An untumbled quartz/methane flask was stored and used as a control for the activation effect.

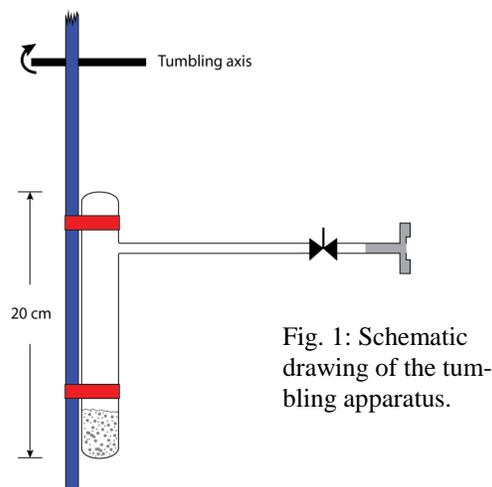


Fig. 1: Schematic drawing of the tumbling apparatus.

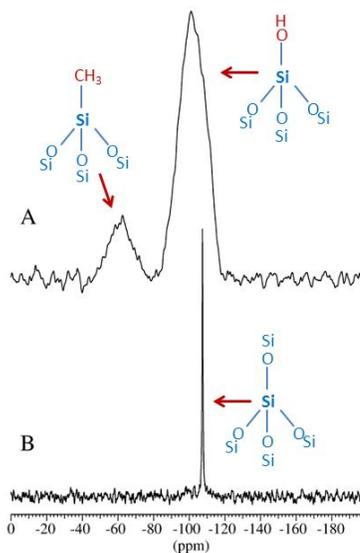


Fig. 2: ²⁹Si MAS and CP/MAS NMR spectra

The standard one-pulse ^{29}Si MAS NMR spectrum of the methane-quartz sample in Fig. 2B exhibits a narrow resonance (FWHM = 0.11 ppm) at $\delta(^{29}\text{Si}) = -107.5$ ppm, *i.e.*, the well-known ^{29}Si chemical shift for α -quartz [5, 6], and thus is assigned to the bulk SiO_2 structure of the sample. More importantly, the ^{29}Si surface sites of the sample are selectively detected in the $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectrum (Fig. 2A), which reveals two broadened resonances at -61 and -101 ppm. The high-intensity resonance at -101 ppm originates from ^{29}Si sites associated with hydroxyl groups, following earlier ^{29}Si CP/MAS NMR studies of silica gels. More importantly, only this resonance at -101 ppm is observed in a similar spectrum of pure quartz exposed to tumbling in ambient air under the same conditions as used for the $\text{SiO}_2/^{13}\text{CH}_4$ sample. Most interestingly, from previous investigations of modified silica surfaces, HPLC materials, and heterogeneous catalysts [7] and [8] it is known that methyl groups directly bonded to a Si atom on a silica surface give ^{29}Si resonances in distinct regions of the ^{29}Si chemical shift scale according to the number of attached methyl groups. For example, for a $(\text{CH}_3)_2\text{Si}(\text{OSi})_2$ species: $\delta(^{29}\text{Si}) = -14$ to -20 ppm, while for $\text{CH}_3\text{Si}(\text{OSi})_3$ species: $\delta(^{29}\text{Si}) = -53$ to -65 ppm. Thus, the observed resonance at -61 ppm can be assigned to a $(\text{SiO})_3\text{Si}-\text{CH}_3$ site. This result and the absence of the resonance at -61 ppm for the tumbled sample of pure quartz present an unambiguous and direct proof that agitation of quartz in a methane atmosphere results in a methyl group being directly bonded to a Si atom on the surface of the quartz particles.

In addition to the $\text{SiO}_2/^{13}\text{CH}_4$ experiments we also tumbled a sample of olivine (from the Canary islands) in ordinary CH_4 (with an isotope distribution of about $^{12}\text{C} = 99\%$ and $^{13}\text{C} = 1\%$). The rate of pressure change for olivine is lower than that for quartz, but not more than a factor of two.

Our laboratory studies show that a wind mediated erosion process of ordinary quartz crystals can produce activated quartz grains, which sequester methane by forming covalent Si-C bonds. If this process is operational on Mars, which our recent preliminary studies on olivine indicate could be the case then it can explain the observed fast destruction of methane.

References: [1] Formisano, V. et al. (2004) *Science*, 306, 1758-1761. [2] Krasnopolsky, V. et al. (2004) *Icarus*, 172, 537-547. [3] Webster, C.R. et al., 2013. *Science*, 342, 355-356. [4] Jensen, S.K.J. et al. (2014) *Icarus*, 236, 24-27. [5] Lippmaa, E. et al. (1980) *J. Am. Chem. Soc.* 102, 4889-4893. [6] Smith, J.V. and Blackwell, C.S. (1983) *Nature* 303, 223-225. [7] Al-

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